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Arsenic speciation in food – current status on standardization of methods for specific determination of inorganic arsenic

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Arsenic (As) is a ubiquitous metalloid found in soils, groundwater, surface water, air, and consequently also in various food items. It is released into the environment from natural sources such as volcanic activity and weathering of minerals as well as from anthropogenic sources including ore smelting, burning of coal, and the use of As-containing pesticides and growth promoters. Arsenic is bioaccumulated in the marine food chain and total arsenic concentrations in the mg/kg range is usually found in marine organisms. Furthermore, arsenic has a quite complex chemistry, especially in the marine environment, where more than 50 different naturally occurring As-containing compounds have been identified, comprising both organic and inorganic forms. Recently, a novel group of lipid-soluble arsenic-containing compounds has been found in marine oils and this group is now added to the list of arsenic compounds (Sele, 2012). Currently research is directed towards characterisation of these compounds in order to obtain a better understanding of arsenic biochemistry in nature. In samples of terrestrial origin the total arsenic concentration is typically < 0.2 mg/kg and the speciation pattern is less complex and in vegetable samples, inorganic arsenic (iAs) usually dominates. In meat and meat-product the total arsenic concentration is usually low (<0.02 mg/kg). However, in certain cases concentrations up to 1 mg/kg have been reported (EFSA 2009).

The various arsenic species have very different toxicities. The organic forms are mainly considered to be non-toxic, whereas inorganic arsenic is highly toxic and exposure may lead to severe adverse effects including cancer. So when addressing food safety aspects of arsenic intake emphasis is on the exposure to inorganic arsenic. Recently, scientific opinions on arsenic in food were issued by the European Food Safety Authority (EFSA 2009) and the FAO/WHO Joint Expert Committee on Food Additives (WHO 2011), focusing on dietary iAs exposure. Both evaluations provided estimates of toxicological intake limits for iAs as a Benchmark Dose Level (BMDL), 0.3–8 $\mu\text{g}\cdot(\text{kg}\cdot\text{bw})^{-1}\cdot\text{day}^{-1}$ for cancers of the lung, skin and bladder as well as skin lesions (EFSA BMDL₀₁) and 2–7 $\mu\text{g}\cdot(\text{kg}\cdot\text{bw})^{-1}\cdot\text{day}^{-1}$ for lung cancer (JECFA BMDL_{0.5}). Due to limited specific data on the content of iAs in food, several assumptions were made to estimate the iAs content on the basis of the total As content in the foodstuff. Hence, in both reports, an urgent need for further data on iAs in food commodities was called upon in order to improve the background data for future risk assessment analysis. Hence, the organisations also called upon further initiatives towards development of validated methods for specific and selective determination of inorganic arsenic in various types of foodstuffs.

Rice and ricebased products have been identified as commodities with relative high concentration of inorganic arsenic (typically in the 0.05 – 0.3 mg kg⁻¹ range) and is one of the most significant contributors to dietary exposure to inorganic arsenic. In the recent years, several national food authorities throughout the World have initiated monitoring programmes on rice and ricebased

products in order to improve risk assessment. Currently, China is the only country that has implemented a maximum level on inorganic arsenic in rice in their national legislation (at 0,15 mg kg⁻¹). However, there are ongoing discussions in both regi of the European Commission and in CODEX Alimentarius on potential future regulation on inorganic arsenic in rice and ricebased products. A maximum level at 0,2 mg kg⁻¹ has been proposed, but this has not been implemented in the legislation (CODEX, 2012).

Although rich in arsenic, seafood in general only contributes very little to the dietary intake of inorganic arsenic. The majority of arsenic in seafood is present in the less toxic organoarsenic forms and the inorganic arsenic concentration is typically lower than 0,1 mg kg⁻¹ in fish samples (Julshamn, 2012). In other types of seafood, however, higher concentrations have been reported, e.g. in bivalve mussels, where concentrations up to 5 mg kg⁻¹ have been seen (Sloth, 2008). Also certain types of seaweed (but not all) may contain elevated levels of inorganic arsenic (in the mg kg⁻¹ range) and thus contribute significantly to the exposure even at low intake.

The increased focus on inorganic arsenic in food has led to several initiatives towards development of methods for selective determination of inorganic arsenic in foodstuffs. The EU-RL for heavy metals in food and feed have arranged several interlaboratory studies where the analytical performance for this parameter has been evaluated (de la Calle, 2011 and 2012; Baer, 2011). The results showed that in general there was good consensus between the participating laboratories when analysing rice and plant material. However, for seafood samples, the picture looked different and no consensus between the laboratories was found.

The need for standardised methods has initiated CEN projects aiming at establishing European standards for the determination of inorganic arsenic in food and feed. The TC327 WG4 on trace elements in feed issued in 2012 a method based on SPE and HG-AAS for determination of inorganic arsenic in animal feedingstuffs of marine origin (CEN, 2012). This novel speciation approach was developed at DTU Food and has furthermore been applied to seafood and rice samples (Rasmussen, 2012 and 2013). Currently, a project in regi of CEN TC275 WG10 on Chemical Elements and their species is on-going with the aim to establish a European standard method for determination of inorganic arsenic in food of plant and marine origin. This method is based on HPLC-ICPMS with anion-exchange chromatography following a simple waterbath extraction approach. A collaborative trial was undertaken in 2013 to evaluate the performance of the method and the outcome will be discussed later this year in the next WG10 expert group meeting.

The initiatives mentioned above clearly illustrate the increased focus on inorganic arsenic in foodstuffs in relation to food safety and the need for continuing the efforts towards further development of reliable analytical methodologies for selective determination of inorganic arsenic and generation of more data on the content of inorganic arsenic in foodstuffs. Once such a dataset has been generated a revised risk assessment on the dietary exposure to inorganic arsenic should be initiated.

The presentation will address the following issues:

- Overview on arsenic chemistry in food
- Overview of the content of inorganic arsenic in foodstuffs
- Analytical approaches for specific determination of inorganic arsenic in food
- Current status on standardisation of methods for determination of inorganic arsenic in food

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